

Novel Lanthanide Alkoxides for Fatigue Resistant PLnZT Thin Films

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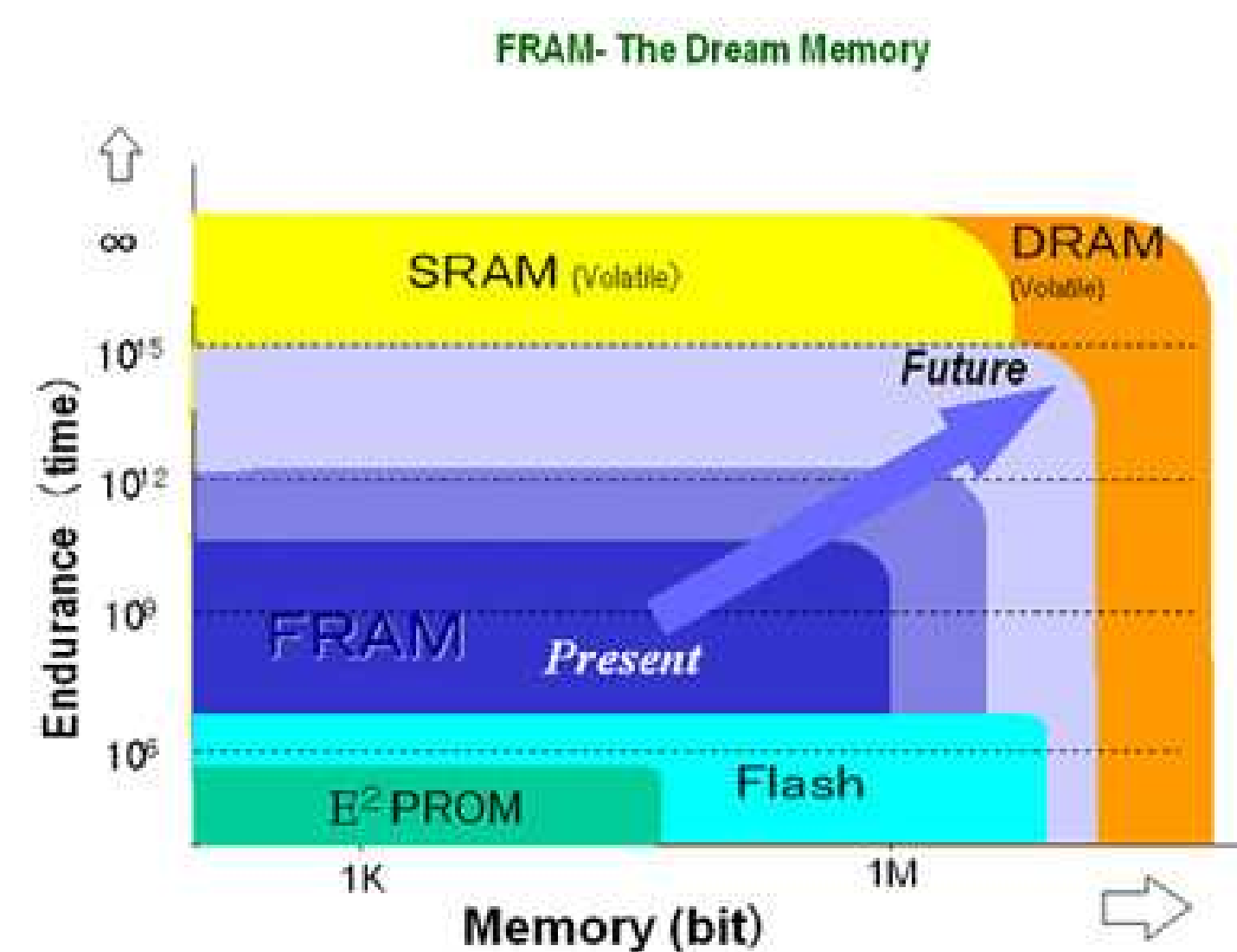
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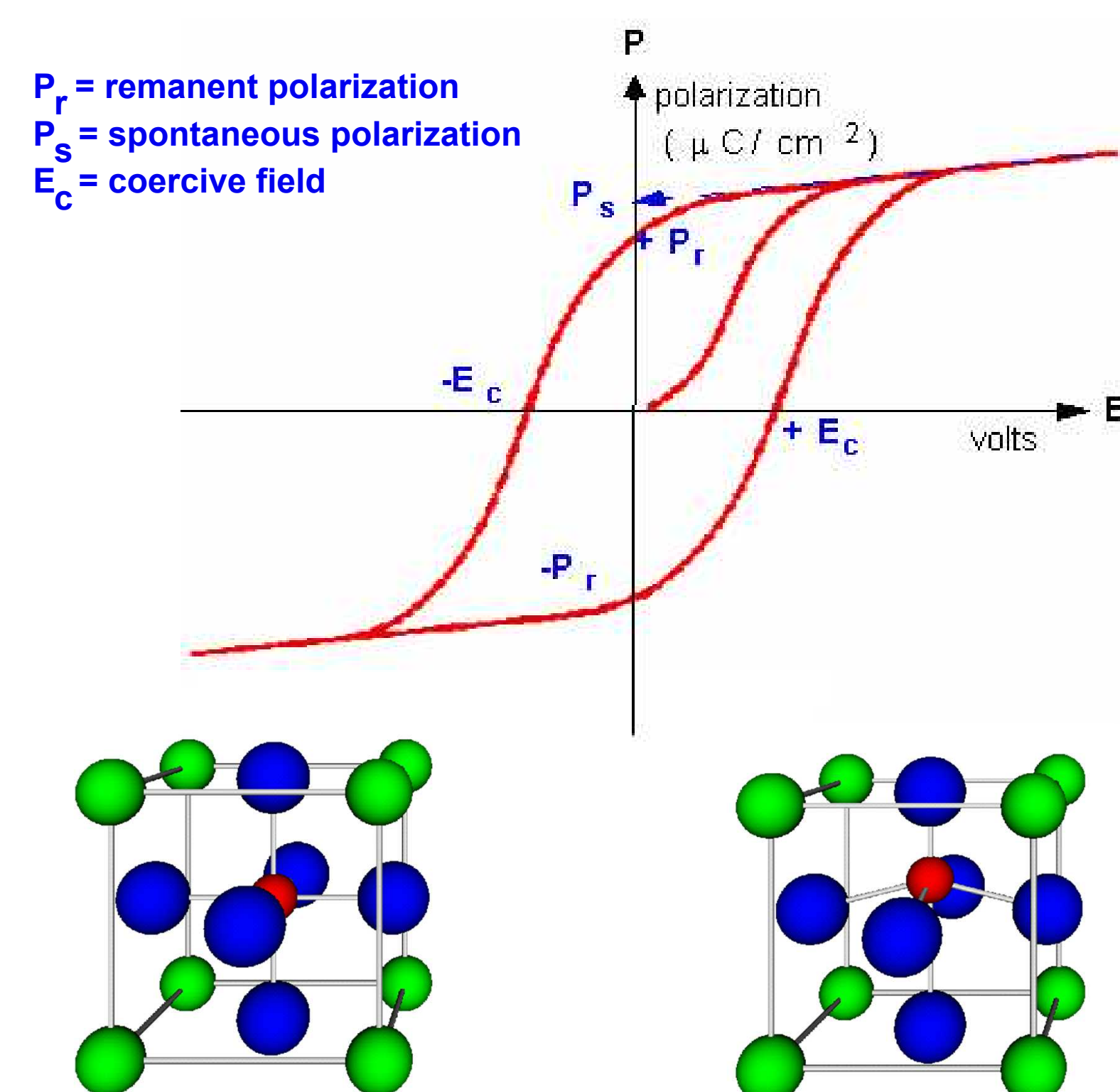


Introduction

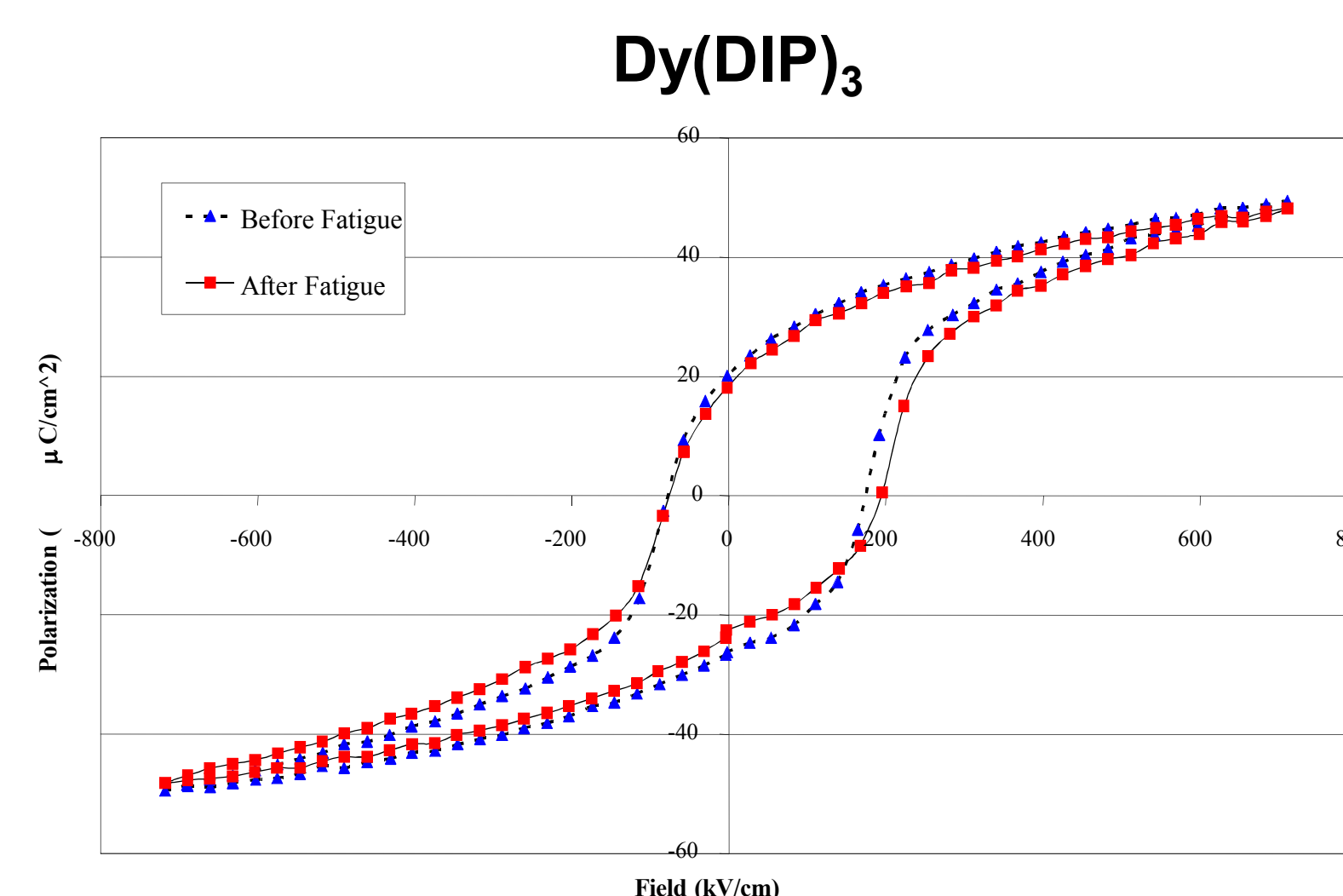
Current computer memories are in need of improvement. Ferroelectric Random Access Memory appears to be the solution. This "Dream Memory" is not only high speed, high security, and hard, it's also non-volatile and has low power consumption.



Ferroelectric materials possess a spontaneous polarization that can be reoriented with an applied electric field which leads to hysteresis in the polarization-voltage response.



Lead Zirconium Titanate (PZT) is a common ferroelectric used in computer memories. However, PZT tends to fatigue (i.e., wear out) over cycle times greater than 10^6 on silica substrates, meaning the B site cation in its perovskite structure stops responding to the electric field as the bond wears out.

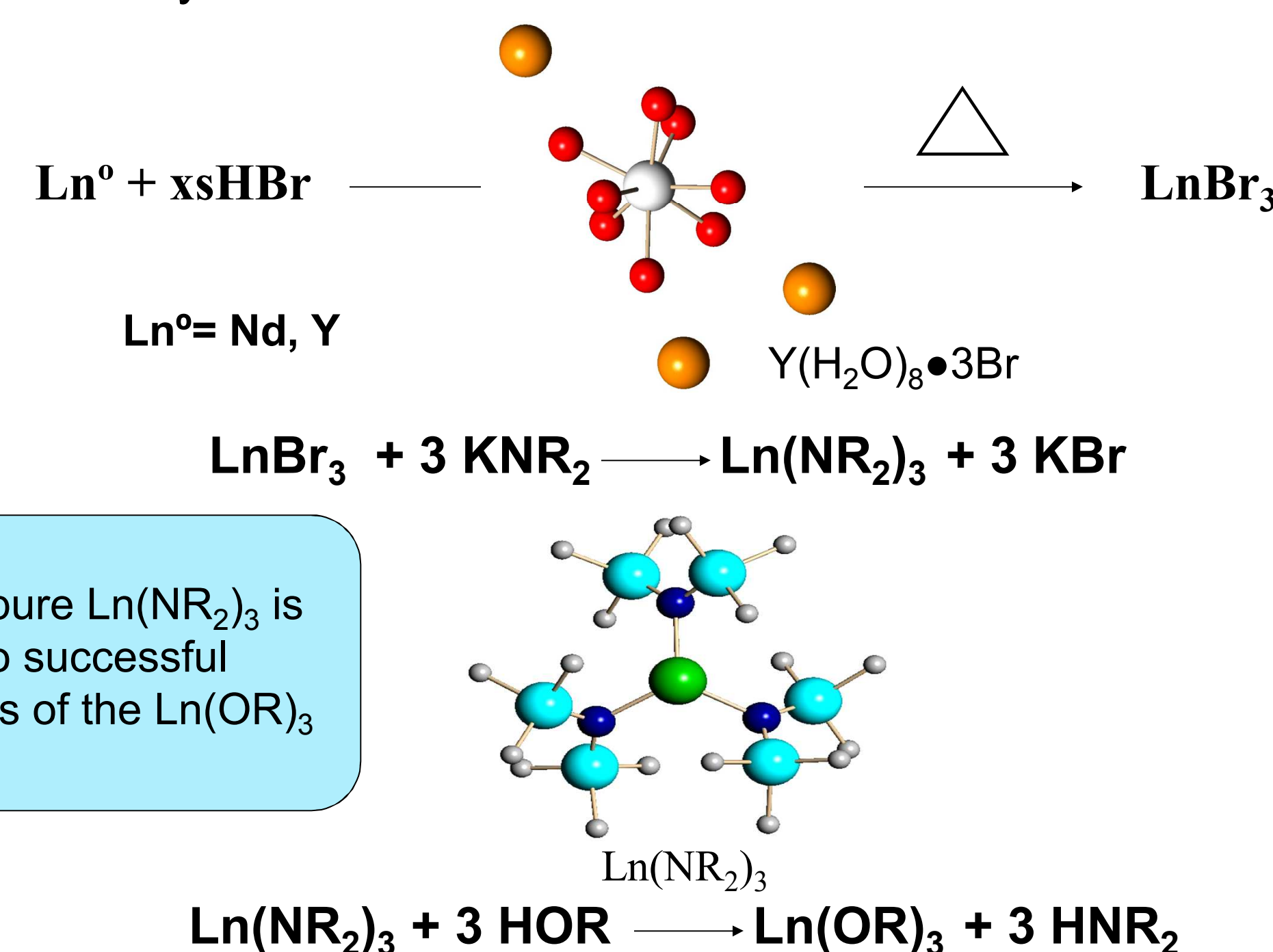


To improve the fatigue behavior of PZT, it is often doped with lanthanum cations but sacrifices polarization. Recently, we have shown that amphoteric lanthanide cations yield fatigue free films with high polarization.

Boyle, T. J., et. al. Inorg. Chem. 2005, 44, 1588-1600

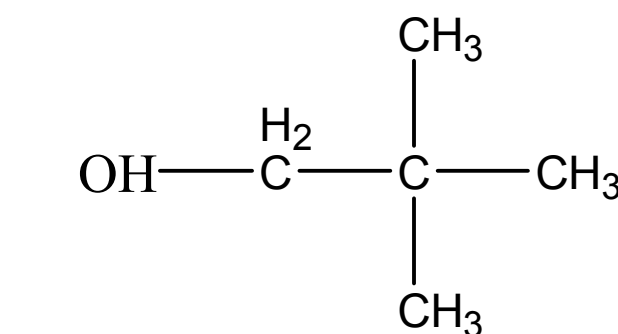
Synthesis of Alkoxides

Lanthanide metals were used to synthesize lanthanide halides that were then used to synthesize lanthanide amides. The amides were reacted with alcohols to synthesize lanthanide alkoxides.



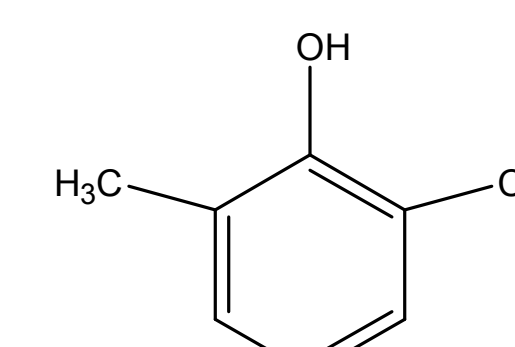
Reactions were run first with an alkyl alcohol, then aryl alcohols, and finally with bidentate alcohols. The alkoxides synthesized will next be used to dope PZT.

Alkyl alcohol:

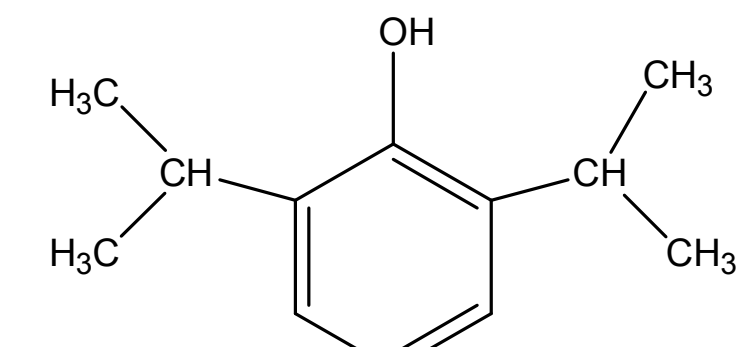


H-ONep neopentyl alcohol

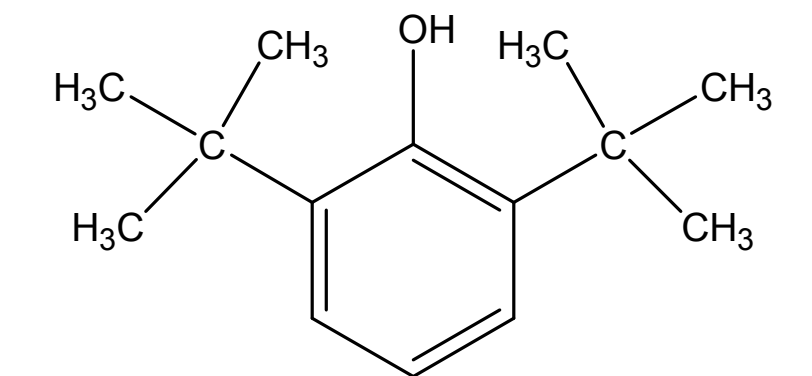
Aryl alcohols:



H-DMP 2,6- dimethylphenol

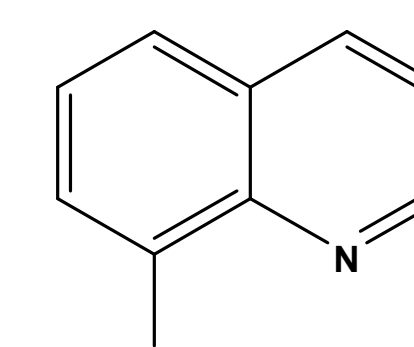


H-DIP 2,6- diisopropylphenol

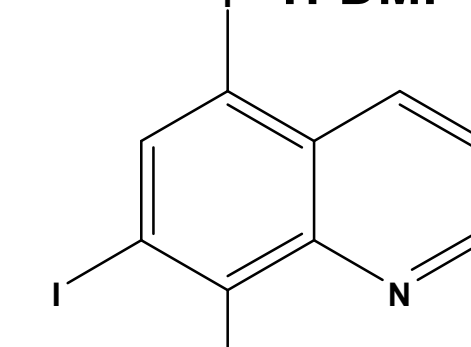


H-DBP 2,6- di-tertbutylphenol

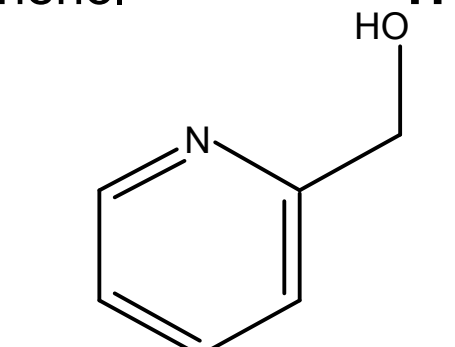
Bidentate alcohols:



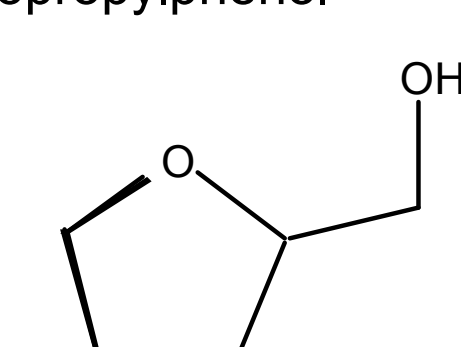
H-HQ hydroxyquinoline



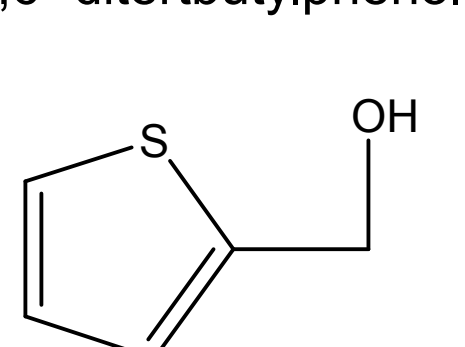
H-IHQ diiodo-8-hydroxyquinoline



H-OPy pyridine methanol



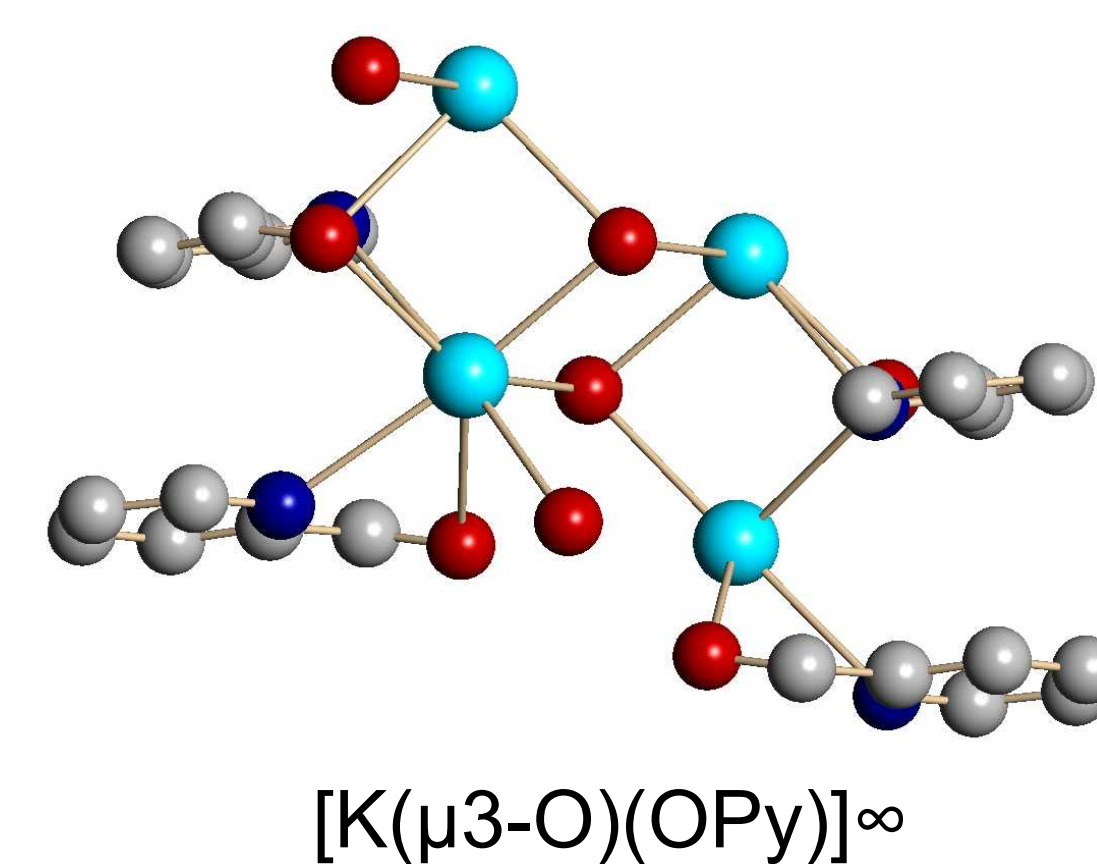
H-OTHF tetrahydrofurfuryl alcohol



H-OTPM thiophenemethanol

Neodymium Alkoxides

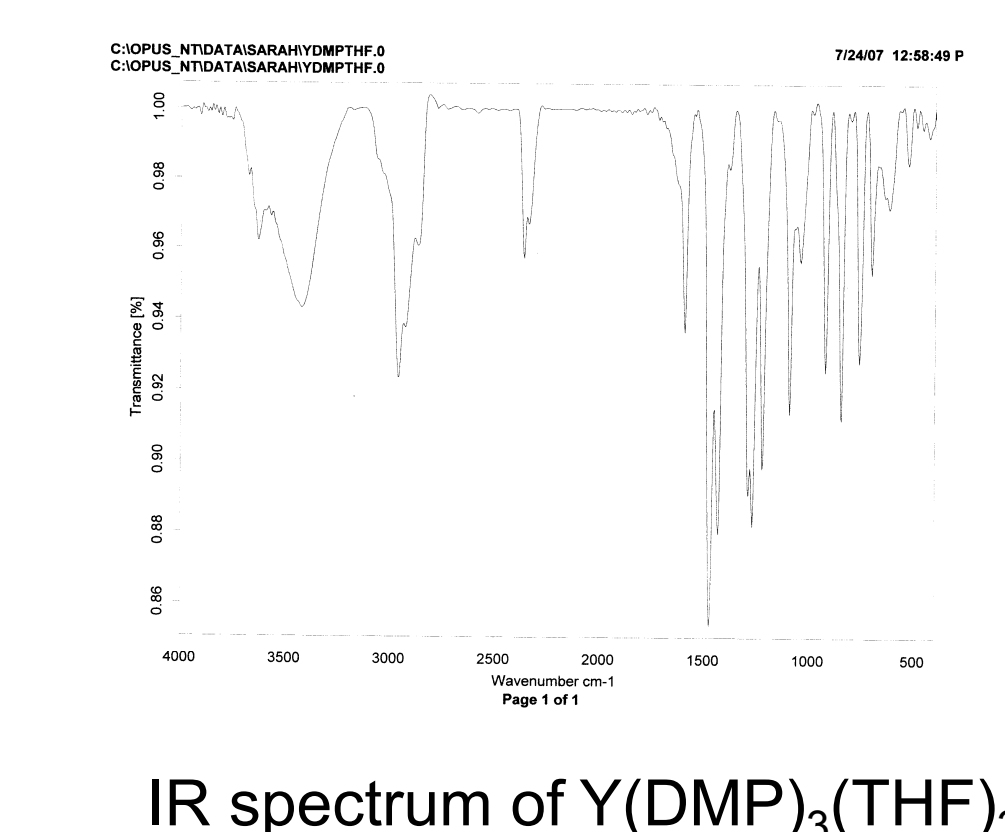
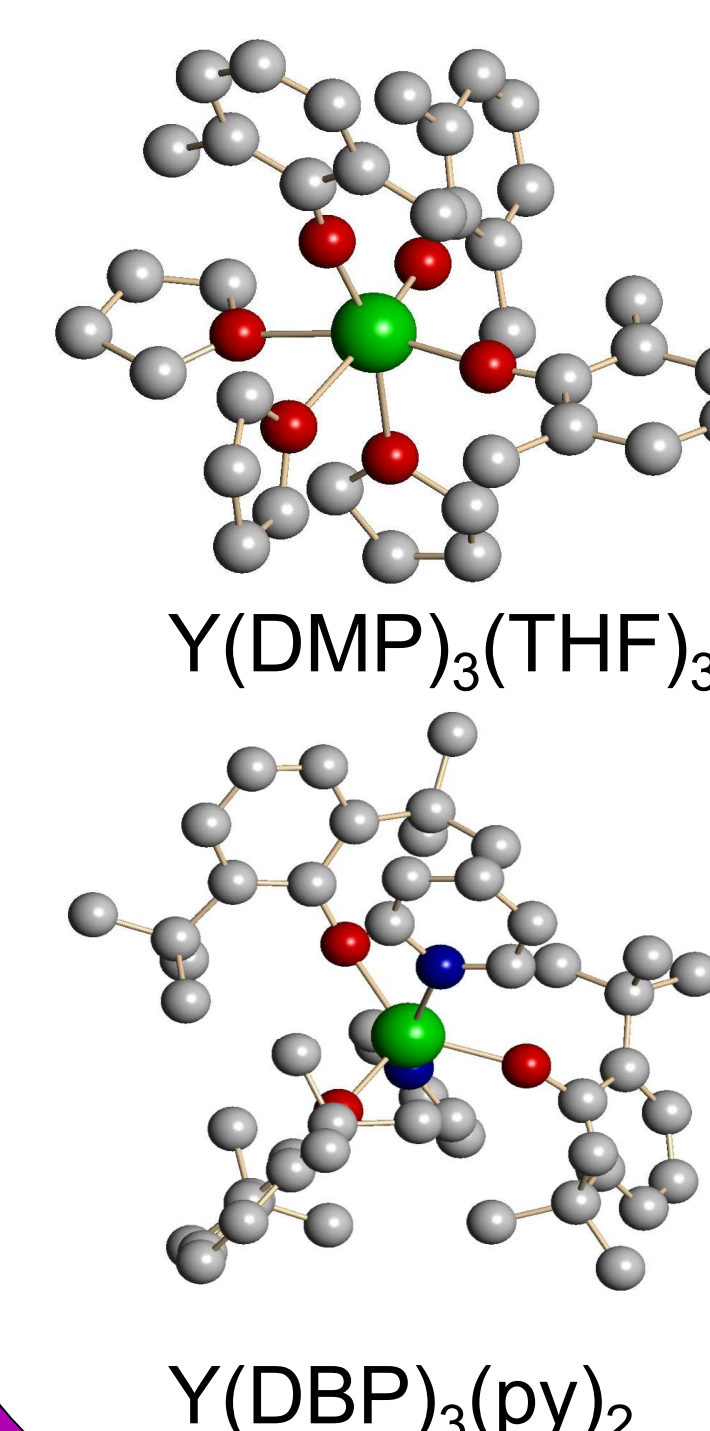
Neodymium was the original lanthanide used, but was found to be extremely hard to purify. Structures contained potassium rather than neodymium.



However, this potassium compound will be useful in other projects and applications.

Characterization of Novel Yttrium Alkoxides

Yttrium was used next as a continuation of previous work. Two novel alkoxides were synthesized and characterized.



NMR spectrum of $\text{Y}(\text{DBP})_3(\text{py})_2$

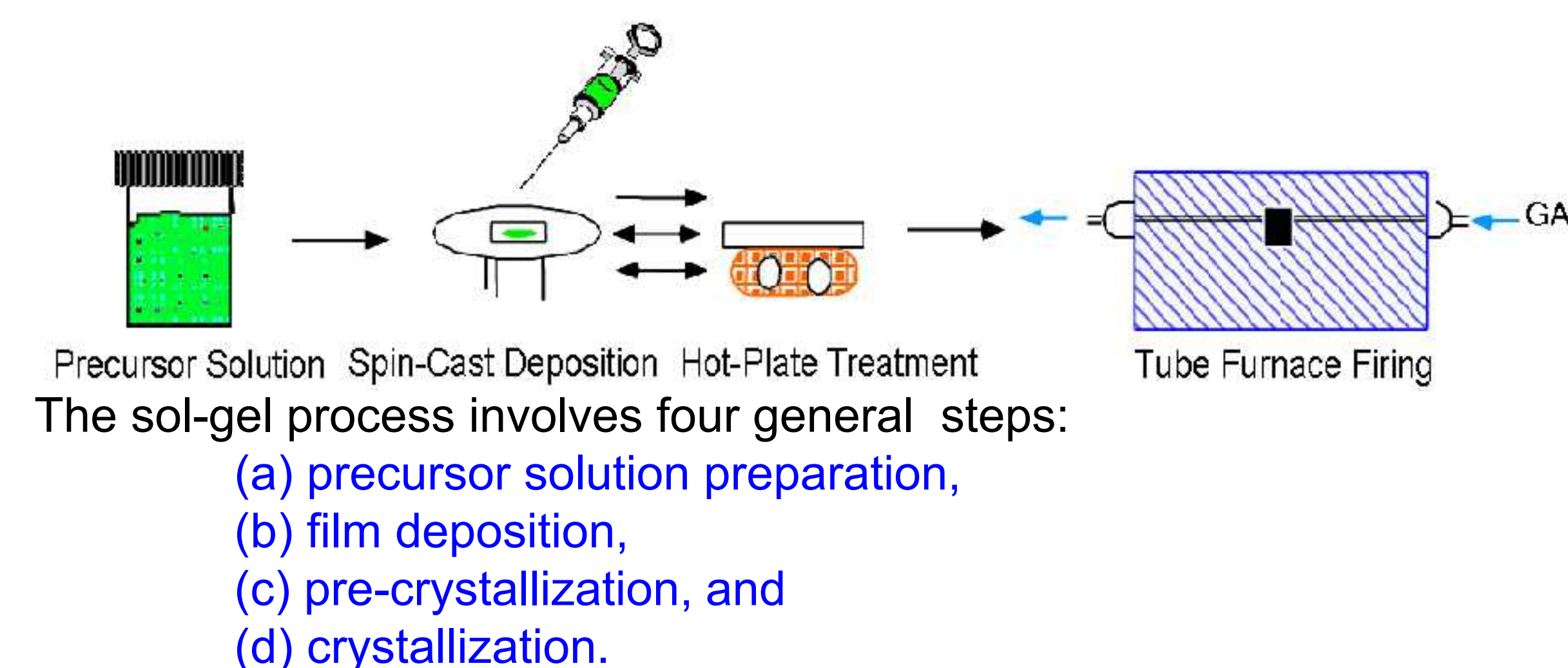
STAR Program

I received this opportunity through the STAR Program and the AP Chemistry teacher at my high school.



Everything in the lab was a new experience. I learned about gloveboxes, schlenk lines, IR, EA, NMR, and Single Crystal X-ray along with basic lab techniques.

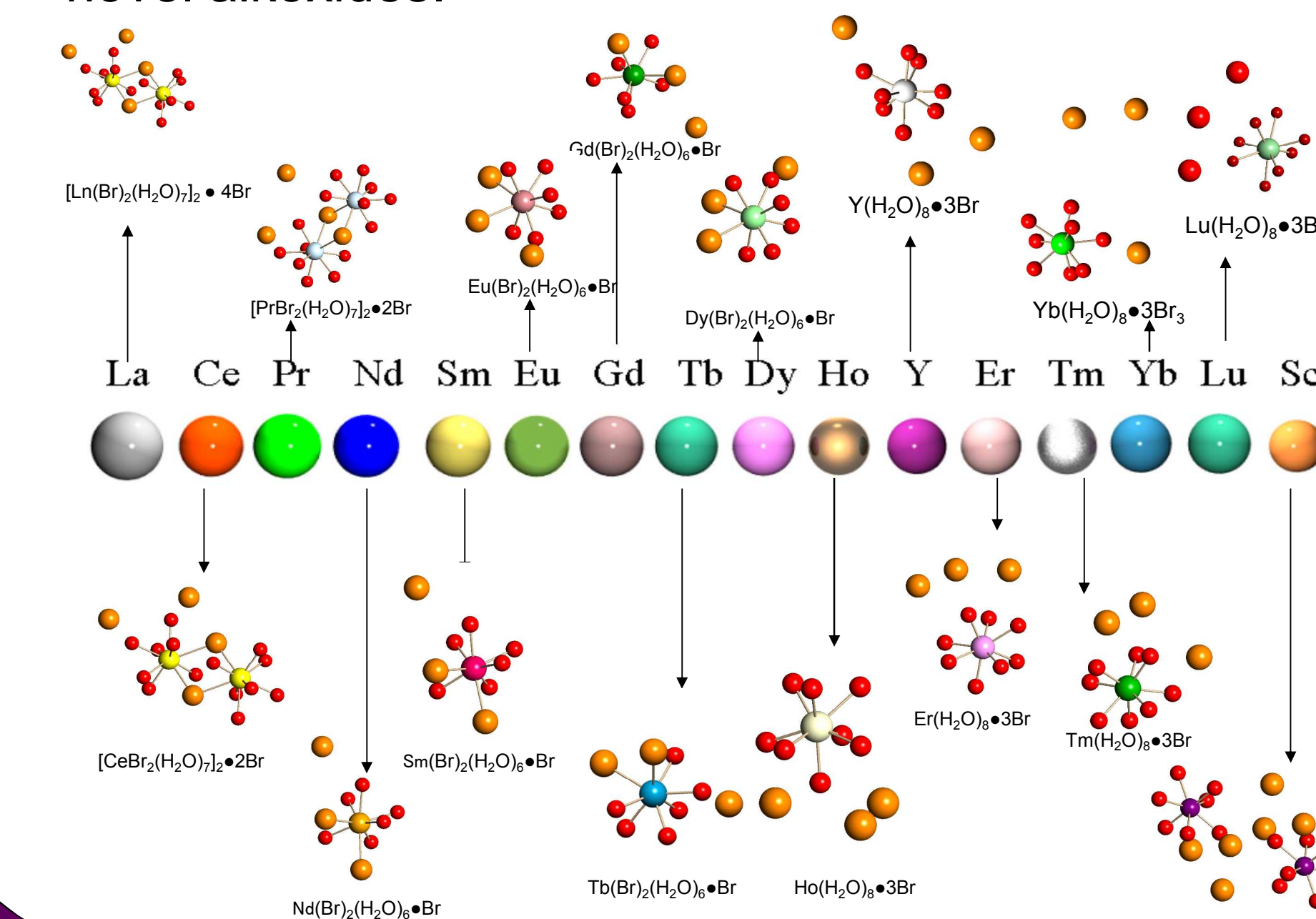
Sol-Gel Method for Making Thin Films



- Multi-layered films spin-coat deposited, in air onto Pt-coated SiO_2/Si substrates using a photoresist spinner (3000 rpm for 30 sec.).
- After each deposition films baked on a hot-plate (300 °C for ~ 5 min.)
- After desired number of layers, the films are fired at 650 °C in a tube furnace for final crystallization.
- All film crystallinity will be verified by XRD.

Lanthanide Halides

To take advantage of the lanthanide contraction and find the best lanthanide dopant we've synthesized halides with Gadolinium, Holmium, Lutetium, and Praseodymium. These will be used to synthesize more novel alkoxides.



Summary

- Goal is to find best lanthanide dopant for PLnZT
- Neodymium is hard to purify and use in alkoxide synthesis
- Yttrium alkoxides were easier to synthesize
- Those novel alkoxides will be used to dope PZT and test fatigue

Acknowledgements

This work supported directly by the Department of Energy - Office of Basic Energy and Science and the United States Department of Energy under contract number DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.